Low Temperature Characteristics of ZnO Photoluminescence Spectra

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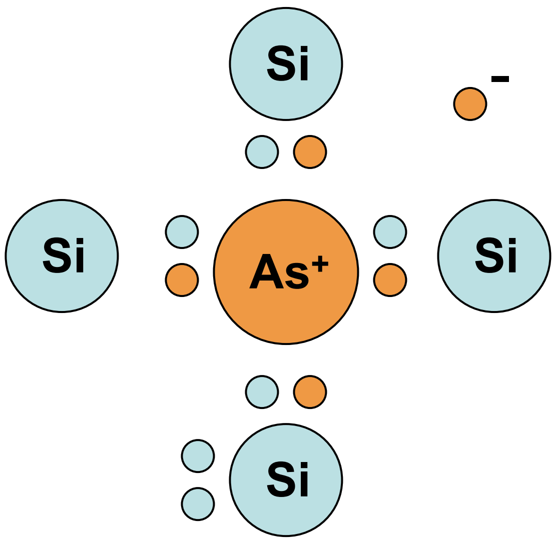
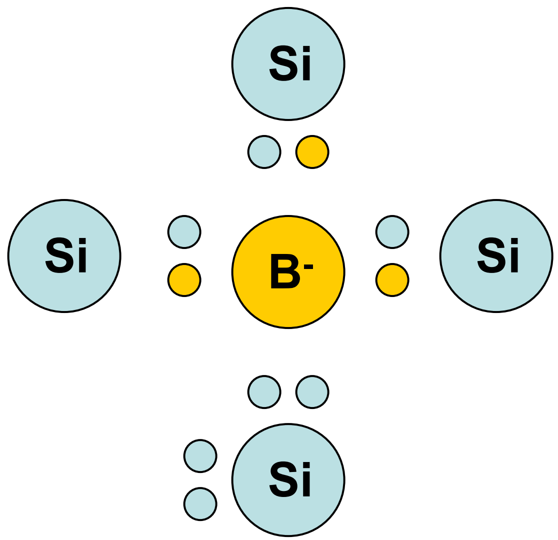
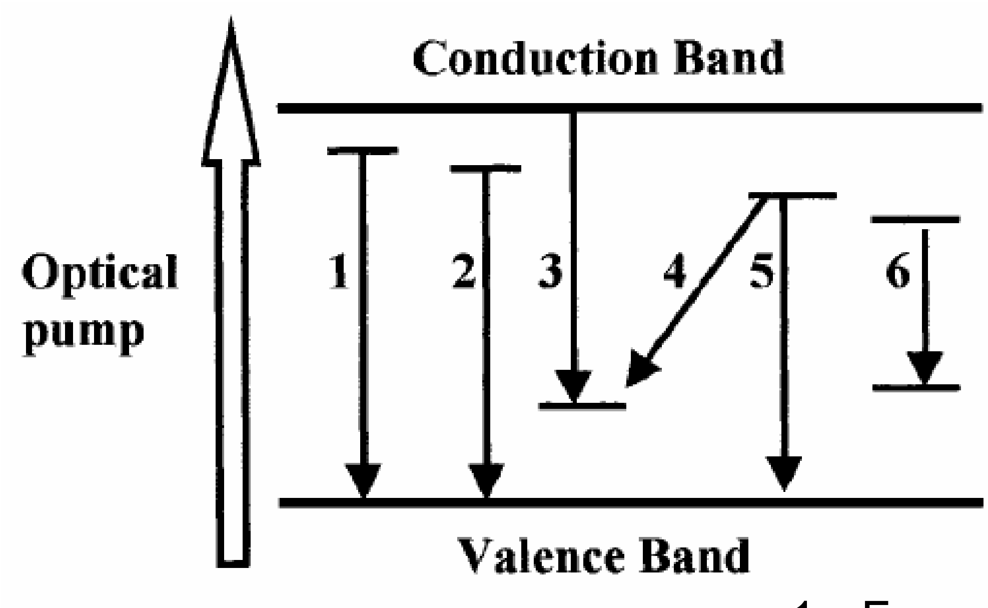
Background

- ***Semiconductors*** are materials that are insulating at absolute zero temperature, but are conducting as temperature is raised or impurities are added (i.e., Si, Diamond, GaAs.)
- ***N-type semiconductor***, negative charge carrier (i.e., Si doped with As, the ***donor***).
- ***P-type semiconductor***, positive charge carrier (i.e., Si doped with B, the ***acceptor***).





Photoluminescence



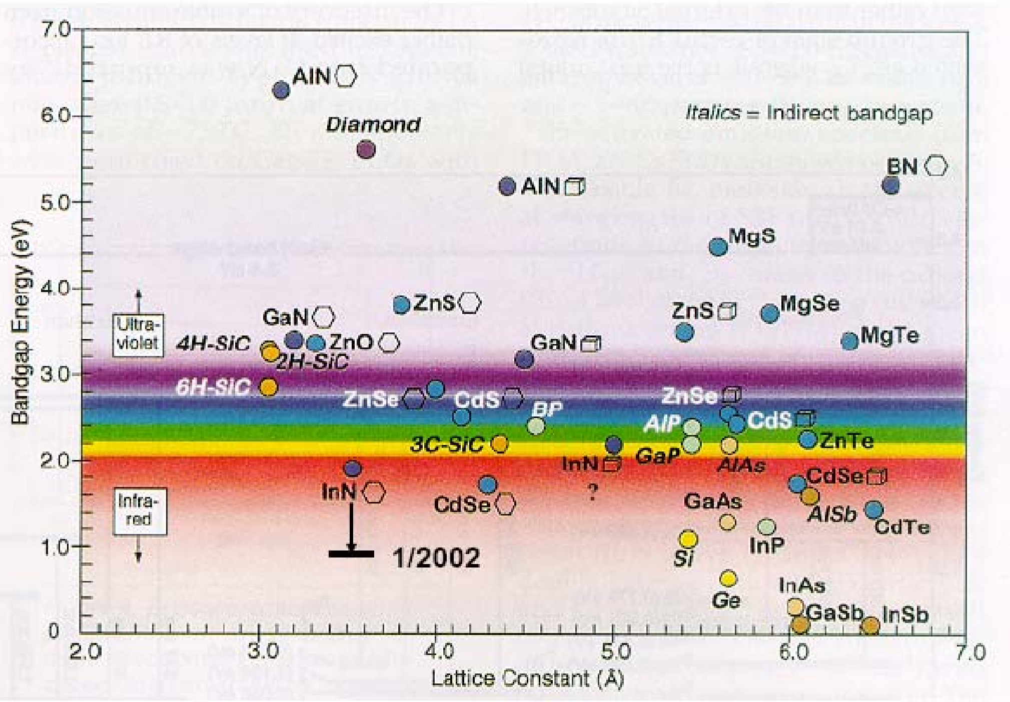
Henry *et al,* **Hyperfine Interactions** (2000)

If the material is excited by an optical beam at an greater than the band gap, electron-hole pairs called the ***exciton*** created.

1. Free excitons (FE or X), denoted by ☝$_{x}$.
2. Bound excitons (BE, DX,AX), denoted by I_{x}.
3. Electron to acceptor.
4. Hole to donor.
5. Donor to acceptor.
6. Other internal impurity of defect transitions.

Some Properties of ZnO

- Wide band gap (3.3 eV) with a high exciton binding energy (60 meV, in comparison to 24 meV for GaN), a bright emitter. Applications in room temperature LDs and LEDs.
- Can easily grow very high quality films.
- As of yet, only n-type materials could be consistently produced. Attempts are made to grow p-type ZnO using N or Li.
- Impurities include In, Ga, H, Al.



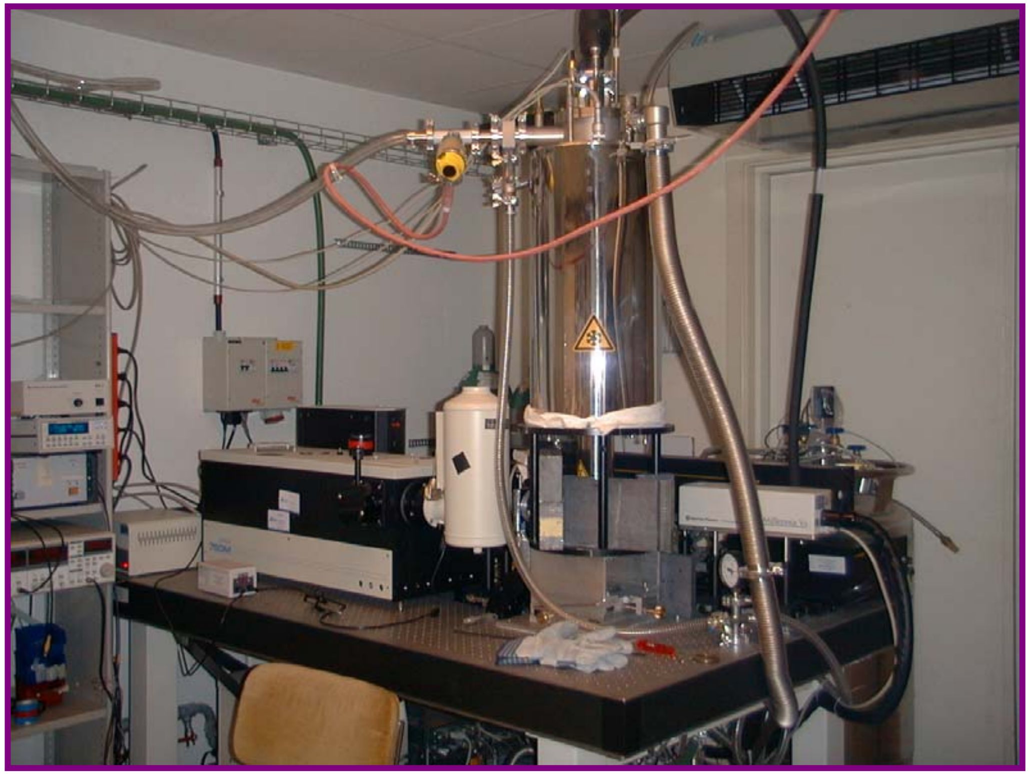
Setup I: Impurity Implantation at ISOLDE

1. 1.4 GeV proton beam hits target, creating radionuclides.
2. The beam goes through a series of magnets, separating out the desired isotopes.
3. Beam enters high energy platform, where it is accelerated to 260 keV and implanted.
4. Greater than 600 isotopes of 60 elements could be created at ISOLDE.

Experiments carried out at ISOLDE, CERN (Isotope Separation Online)
Hyperfine Interactions: 129 (2000)

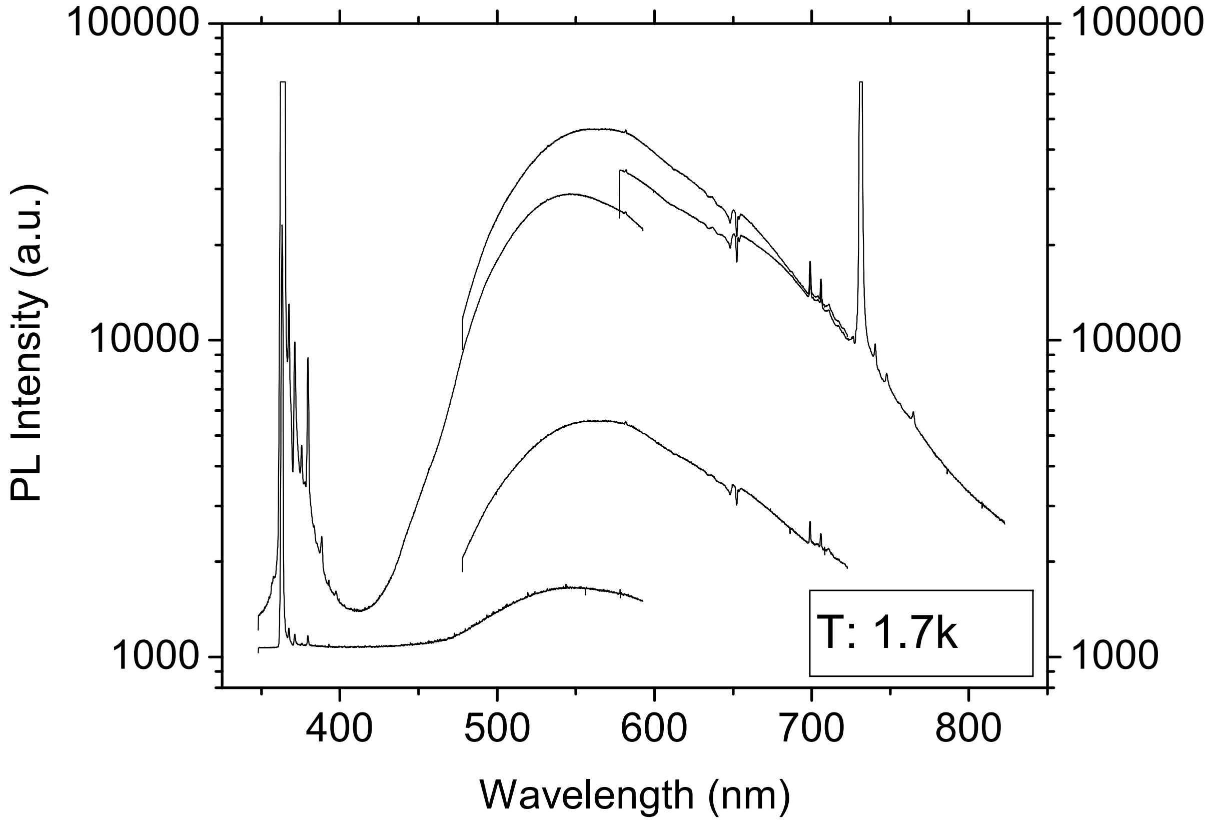
Setup II: APRIL
(*Apparatus for Photoluminscence Investigations with Radioactive Isotopes off-Line*)

1. A HeCd laser operated at 325 nm is used to excite the sample at an energy above the band gap.
2. The sample is immersed in liquid He, to keep the surrounding temperature around 2K.
3. The PL signal enters the monochromator, and a CCD camera cooled by liquid N is used to convert the signal into electronic signal.
4. The data is then transferred to a computer for analysis.

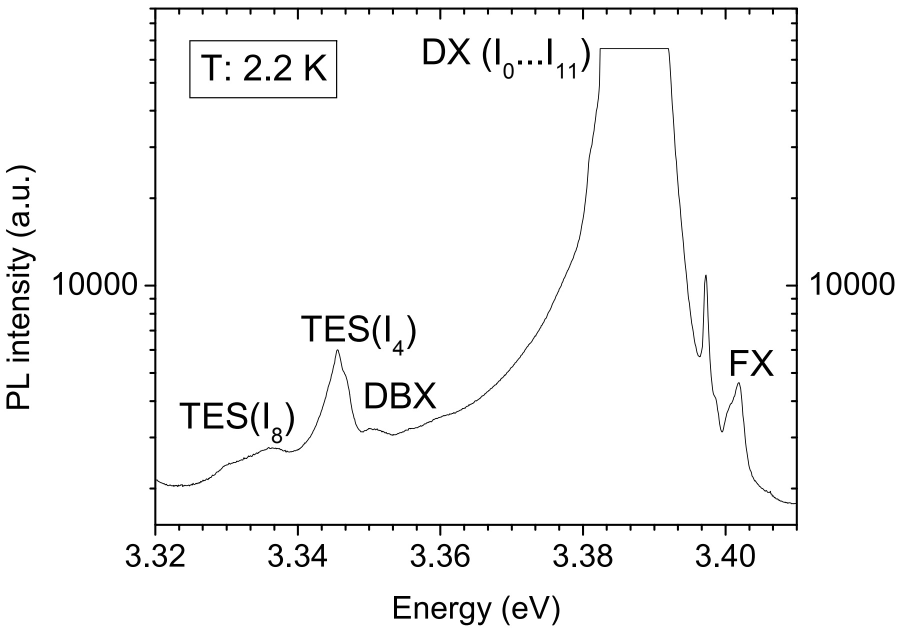


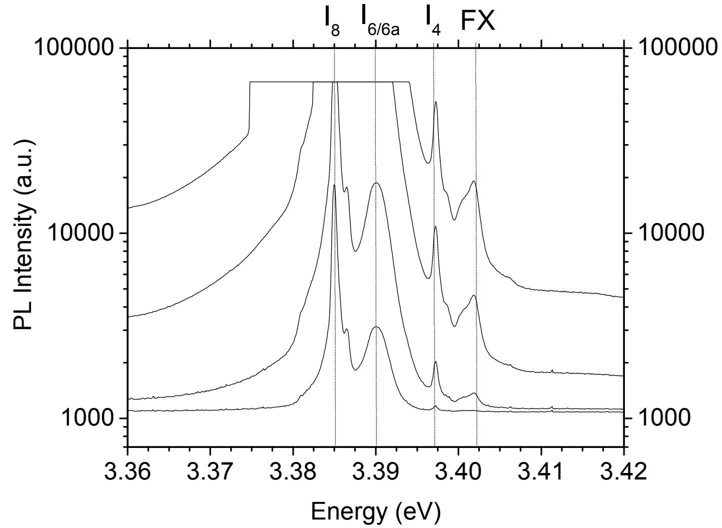
Undoped ZnO on Rubicon

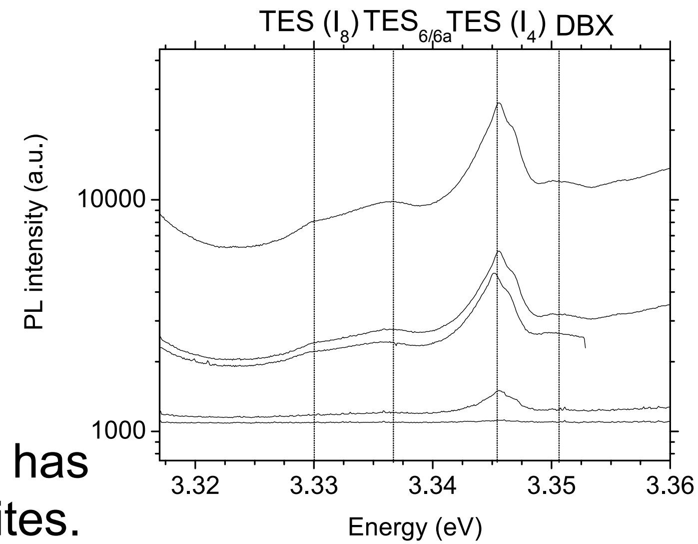
- The most prominent peaks are at the far left, representing the shallow bound excitons.
- They are preceded by three smaller FE lines, conventionally denoted by A, B, and C.
- The red is occupied by a distinctive broad band, called the ***Green band***, due to maybe Cu impurities, or Zn or O vacancies.



Bound Excitons and Two Electron Satellites







- Through diffusion experiments, they have been attributed to shallow impurities such as H(I_4), Al(I_6), Ga(I_8), and In(I_9).
- Between the BE and TES lines is the DBX peak. Using catholuminescence techniques, it has been attributed to structural defect recombination sites.

Some Properties of ^{73}Ga

- A group III element, proven good n-type dopants for ZnO.
- 1.26 Å covalent radius, similar to the 1.31 Å for Zn.
- Neutron rich, decays via beta emission:

$$^{73}_{31}Ga \longrightarrow ^{73}_{32} Ge + ^{0}_{-1} e + ^{0}_{0} \bar{\nu}.$$

•Lifetime of 4.86 hours, with a decay energy of 1.59 MeV.

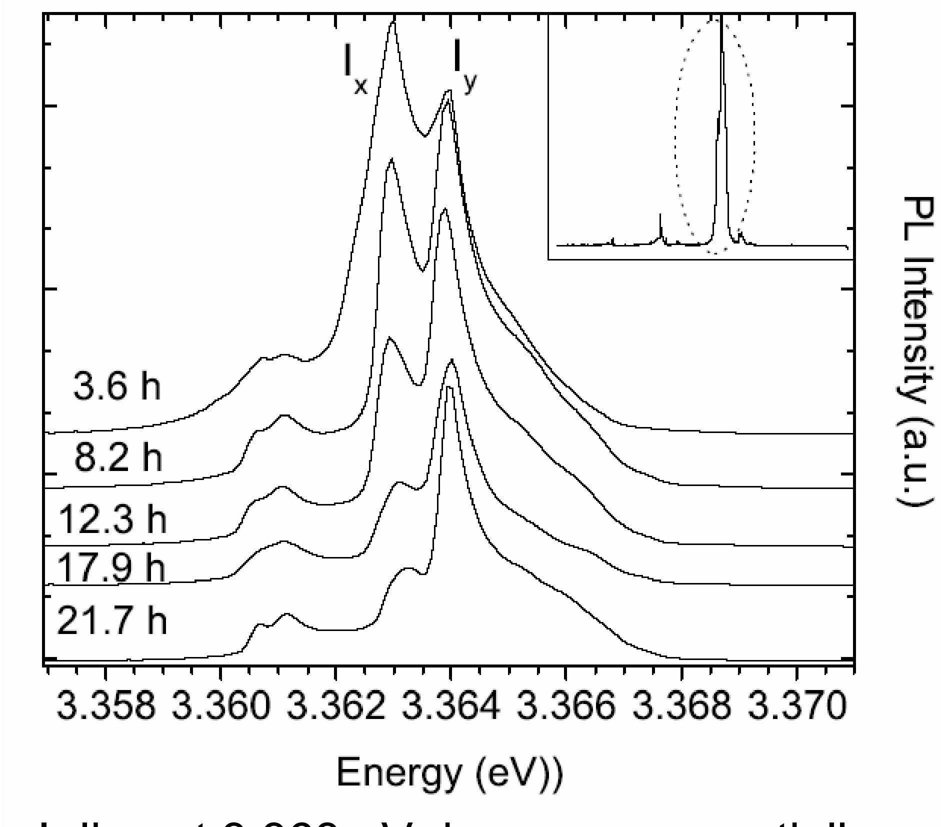
•Dopant concentrations are given by:

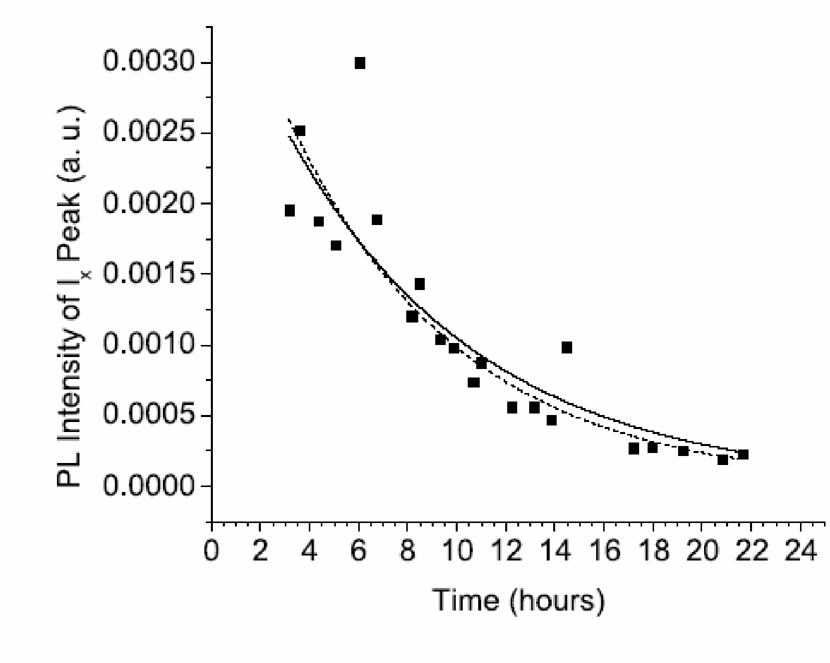
$$[Ga](t) = [Ga](0)e^{-\lambda_{Ga}t}$$

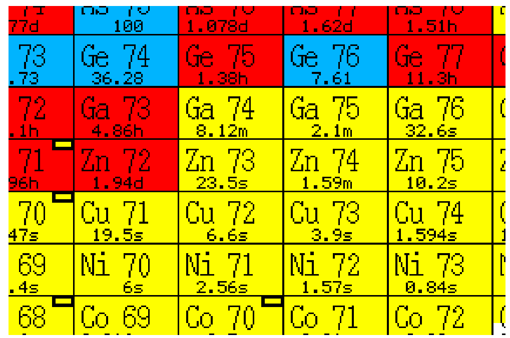
$$[Ge](t) = [Ge](0)(1 - e^{-\lambda_{Ga}t})$$

where $\lambda = \ln(2)/t_{1/2}$.

^{73}Ga Doped ZnO

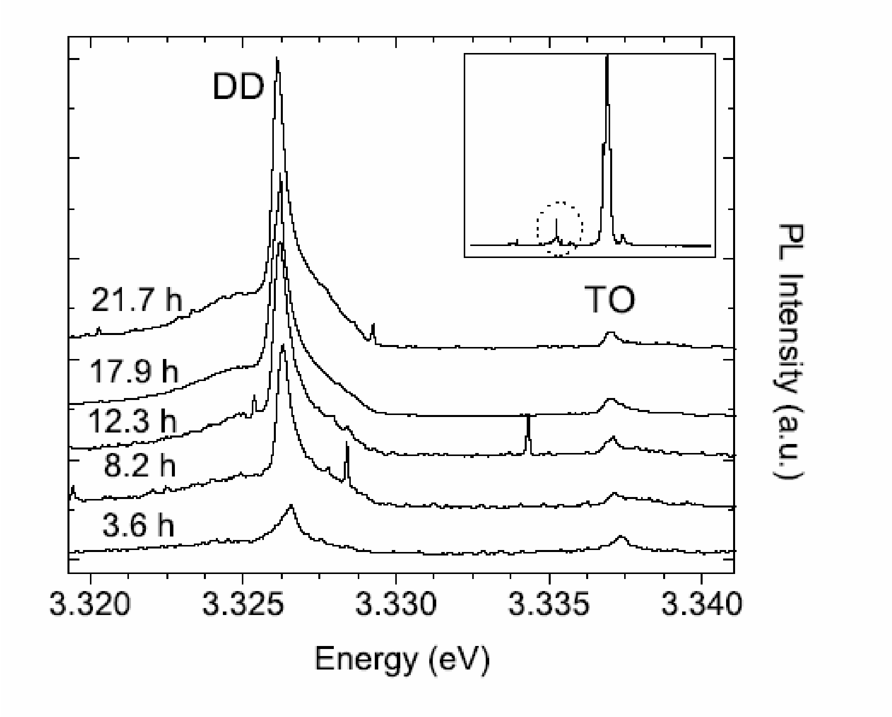


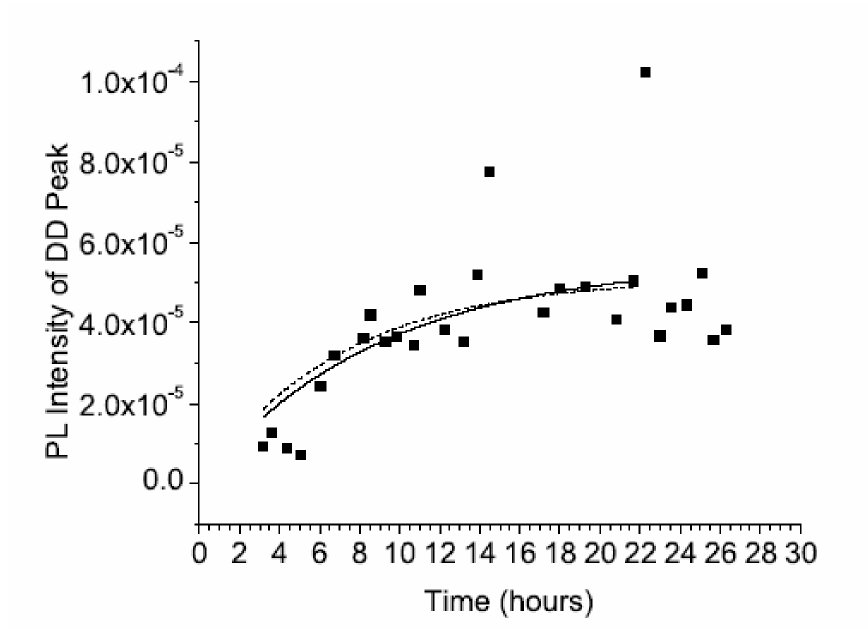




- I_x line at 3.363 eV decays exponentially.
- I_y line at 3.364 eV remains the same.
- Phonon line at 3.337 eV used to normalize all peaks.
- Exponential fit gives a half-life of 5.5 hours, with 17.5% uncertainty.

^{73}Ga Doped Sample at Lower Energies





- DD line at 3.326 eV grows as time progresses.
- Exponential fit of normalized intensity gives a half-life of 5.3 hours with 27% uncertainty.
- Same line also observed in stable Zn implanted samples at a slightly different energy.
- The line might be due to interstitial defects, or the ^{73}Ge dopant.

Some Properties of ^{107}Cd and ^{107}Ag

- Cd is isoelectronic to Zn.
- Ag introduces deep acceptor levels in group II-VI semiconductors such as CdTe and ZnTe.
- ^{107}Cd is neutron poor, decays via electron capture:

$$^{107}_{48}Cd + ^{0}_{-1}e \longrightarrow ^{107}_{47}Ag + ^{0}_{0}\nu$$

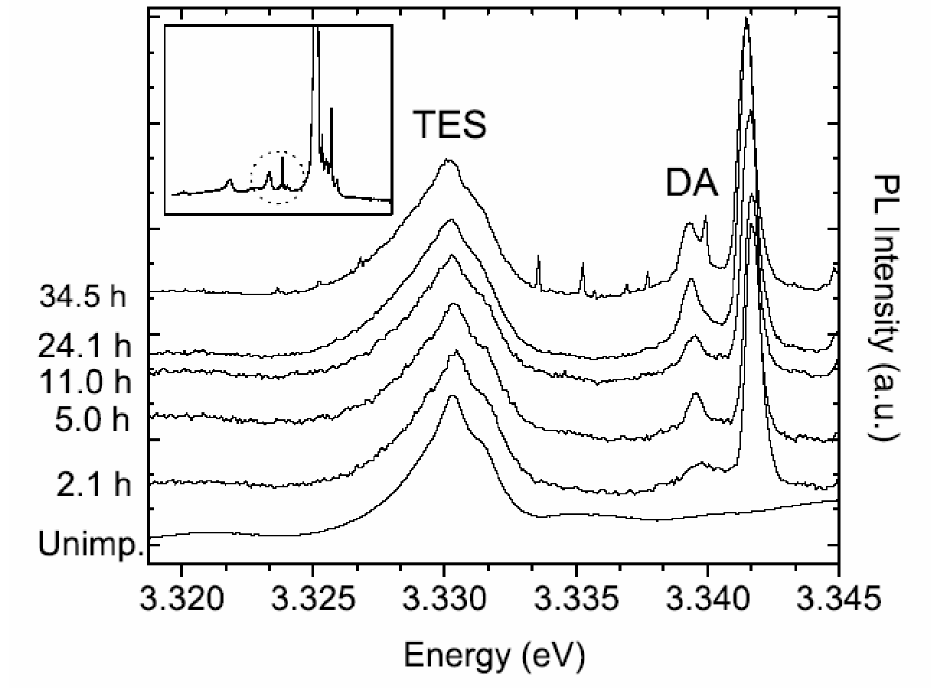
• ^{107}Cd has half-life of 6.5 hours, with a decay energy of 1.42 MeV.

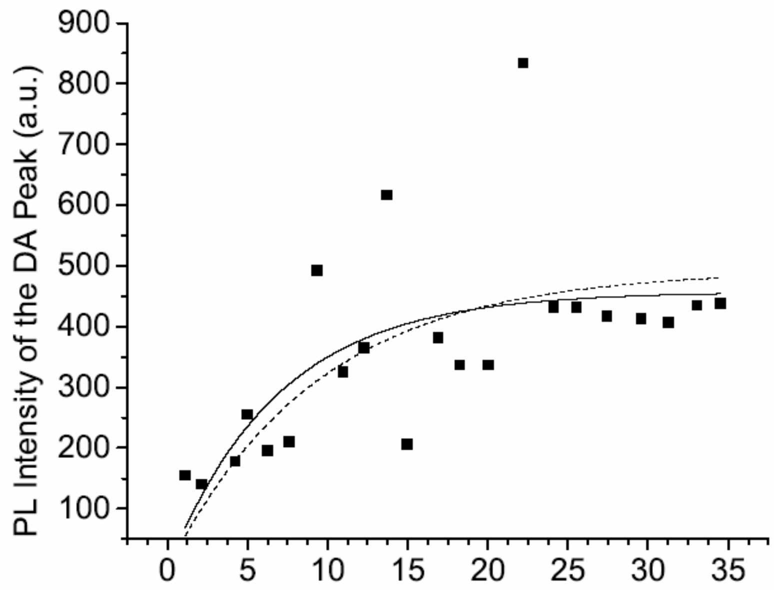
• Concentrations of the dopants are given by:

$$[Cd](t) = [Cd](0)e^{-\lambda_{Cd}t}$$

$$[Ag](t) = [Ag](0)(1 - e^{-\lambda_{Cd}t}).$$

^{107}Cd Doped ZnO



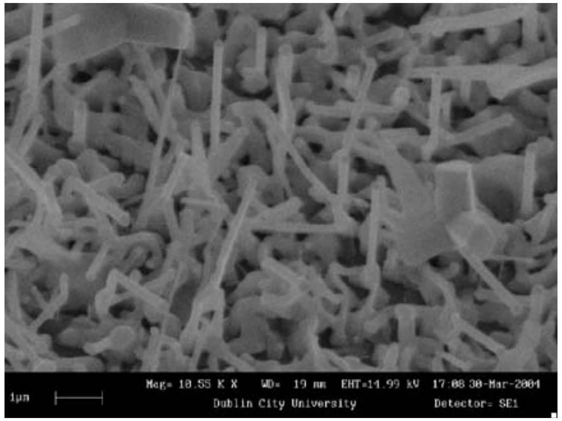


- No lines with a systematic decay, which could be attributed to ^{107}Cd.
- TES(I_4) line at 3.330 eV remains constant, used to normalize all peaks.
- DA line at 3.340 eV grows exponentially.
- Exponential fit of the Normalized intensity of this line gives a half-life of 5.3 hours with 19% uncertainty.

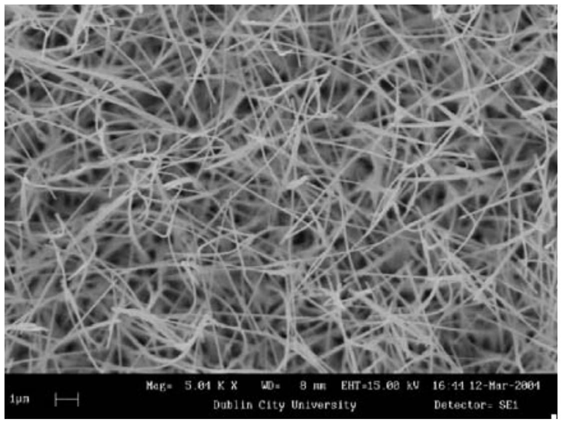
Sn107 2.9m	Sn108 10.3m	Sn109 18m	Sn110 4.11h
In106 6.2m	In107 32.4m	In108 58m	In109 4.2h
Cd105 55.5m	Cd106 1.25	Cd107 6.5h	Cd108 0.89
Ag104 1.15h	Ag105 41.29d	Ag106 8.28d	Ag107 51.839

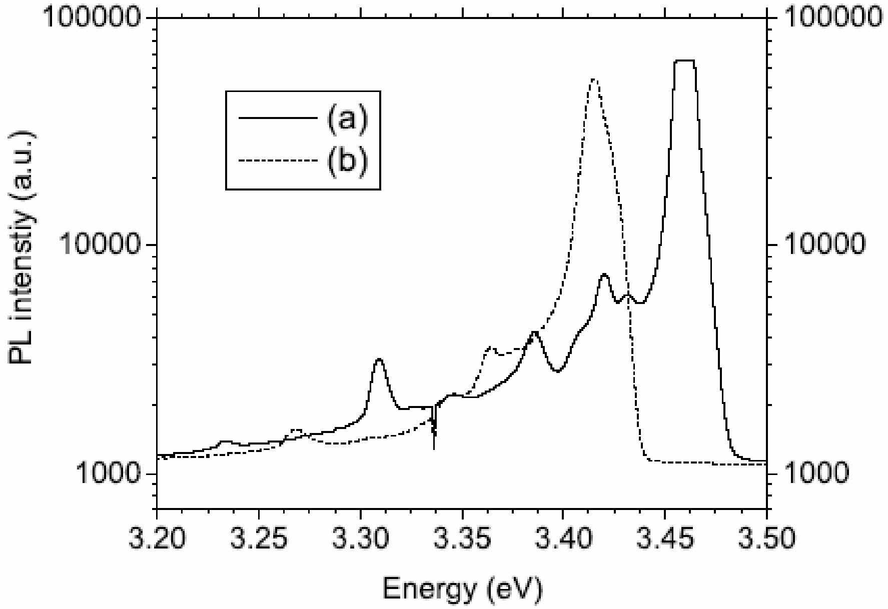
ZnO Nanorods

Sample A (grown with 20 Å Au catalyst).



Sample B (grown with 52 Å Au catalyst).





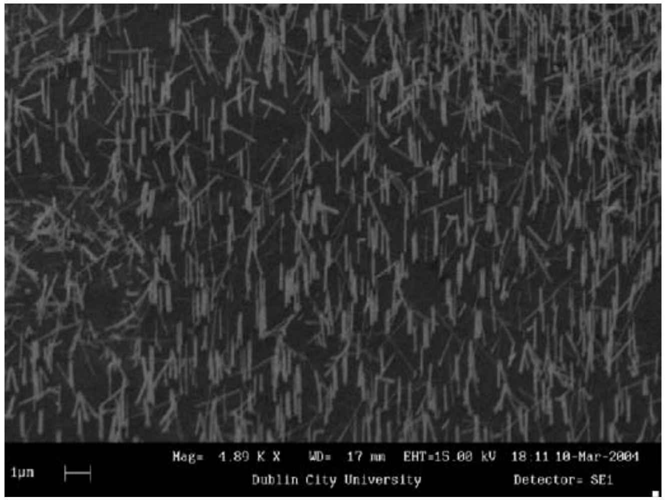
•PL of sample B red shifted from that of sample A, indicating quantum confinement.

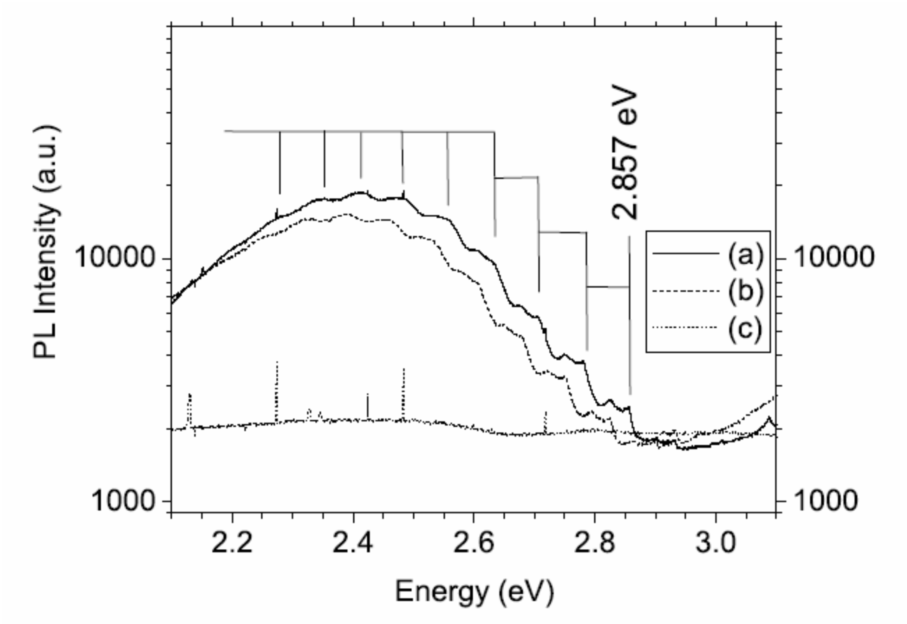
•Higher Au catalyst concentration increases nanorod radius.

Grabowska *et al.,* Dublin City University.

Green band of ZnO Nanorods

Sample C. Aligned Nanorods grown with conditions similar to A.





•Green band intensity increases as nanorod radius decreases. Higher vacancy density in thinner nanorods.

•Intensity decreases for sample C. Alignment reduces the percentage of vacancies.

Summary

- A 3.363 eV line is identified as Ga-related and a 3.326 eV line is attributed to Ge or interstitial defects.
- As a potential discovery of a shallow acceptor, the half-life of a 3.340 eV line indicates that it might be Ag-related.
- An increase in Au catalyst concentration during growth increases the ZnO nanorod size.
- An increase green band intensity as radius decreases indicates higher vacancy densities in thinner nanorods.
- Nanorod aligment reduces the percentage of vacancies present.